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Using solid phase microextraction and gas chromatography/mass spectrometry when analyzing fire debris for pseudoephedrine, a prescursor drug in clandestine methamphetamine production

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USING SOLID PHASE MICROEXTRACTION AND GAS CHROMATOGRAPHY/MASS SPECTROMETRY WHEN ANALYZING FIRE DEBRIS FOR PSEUDOEPHEDRINE, A PRECURSOR DRUG IN CLANDESTINE METHAMPHETAMINE PRODUCTION

by

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ABSTRACT

The production of methamphetamine in clandestine laboratories presents a particular hazard due to the environmental hazards it poses. In addition to the dangers associated with using caustic and reactive solvents, these clandestine laboratories also have the potential to cause a fire or explosion. This danger has caused some states to redefine arson to include fires caused by the illicit manufacture of drugs.

Arson investigation can be challenging due to the destructive nature of the crime. Much of the evidence that existed prior the fire can be consumed and evidence that does survive can be difficult to identify in the rubble. Despite these difficulties, methods have been developed to determine the types of accelerants present in addition to identifying illicit substances such as methamphetamine and the precursor drug pseudoephedrine.

This study was designed to determine if solid phase microextraction combined with gas chromatography/mass spectrometry

could be used to analyze burned samples of wood to which pseudoephedrine had been applied. In addition, an experiment was designed to determine what concentration of pseudoephedrine must be present before a fire in a controlled laboratory setting, for a detectable amount to remain. Samples were created by adding pseudoephedrine hydrochloride, either in powder form or dissolved in methanol, to blocks of Douglas Fir and exposing the surface to a flame for two minutes. Additional samples were created by adding trace amounts, i.e. microliter quantities, of pseudoephedrine standard to blocks of wood before placing them in a fire for ten minutes.

A thermal degradation product of pseudoephedrine was detected in samples containing more than 15 mg of the drug. To verify that the detected product was a result of thermal degradation, 10 mg of pseudoephedrine were heated at 200 °C for one hour. The product of the thermal degradation study and the product detected following two minutes of exposure to a flame had the same retention time and mass spectrum. Therefore, it was concluded that the detected thermal degradation product may be used to indicate the presence of pseudoephedrine in a fire.

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LIST OF ABBREVIATIONS

°C	degrees Celsius
µg	micrograms
µL	microliters
FBI	Federal Bureau of Investigation
GC	Gas Chromatograph
ID	Internal Diameter
i.e.	id est – meaning “that is”
in.	inches
IR	Infrared
m/z	Mass to Charge ratio
mg	milligrams
mL	milliliters
MS	Mass Spectrometer
P2P	Phenyl-2-Propanone
SIM	Selected Ion Monitoring
SPME	Solid Phase Microextraction
SWGDRUG	Scientific Working Group for the Analysis of Seized Drugs

1. INTRODUCTION

1.1 Methamphetamine Abuse in the United States

Methamphetamine is a central nervous system stimulant first synthesized in 1919 in Japan(1). In the nearly one hundred years since its first discovery, methamphetamine use has grown from its initial uses in treating asthma to a drug of abuse that one third of law enforcement agencies in the United States reported as their "greatest drug threat" in 2015(2). The danger this compound poses comes from its addictive nature and the dependence potential which led to it being listed as a Schedule II drug under the Controlled Substances Act passed in 1970(3), as well as the hazards associated with its production and distribution.

The abuse of methamphetamine in the United States can be traced as far back as the 1940s when inhalers containing various amphetamine derivatives could be legally obtained(4). By breaking open the inhaler and taking out the filter strips, users could extract the drug or ingest the strips themselves to obtain the desired high(4). As regulations on the drug have changed throughout the years, so has the manner in which it is abused. Methamphetamine can be inhaled, ingested or injected. This versatility has given rise to many forms and many names(5). Among many of the slang terms used to describe the drug are "speed", referencing its stimulant effect; "crank", a term derived

from its distribution by motorcycle gangs; “ice”, the term for the drug when inhaled; and “crystal” in reference to its crystalline structure(6).

Just as the manner for administering methamphetamine changed, so did the way in which it has been distributed. For the first several decades of its abuse, methamphetamine was obtained by diverting supplies that had been legally manufactured into the black market(1). However, by the 1960s a large supply of the drug was being produced in clandestine laboratories(7). Large laboratories, mainly in Southern California and Mexico, produced most of the methamphetamine abused in the United States, however smaller laboratories also existed. The number of these smaller laboratories grew as the demand for methamphetamine rose and information on drug synthesis become more widely available(7). By 2014, most clandestine laboratories discovered in the United States produced only enough product for the manufacturer and a few associates using the relatively new “one-pot” method(2).

Although the majority of methamphetamine available in the United States comes from production laboratories in Mexico, small domestic laboratories pose an additional threat(8). The volatile chemicals; such as Diesel fuel, lighter fluid, brake cleaning fluid, or camping fuel; used during the production of methamphetamine from its precursors are highly flammable and many of the production methods involve reactive

metals. In addition, manufacturers often do not follow safe laboratory practices which can lead to chemical fires or explosions.

1.2 Methamphetamine Production in the United States

The illicit production of methamphetamine in the United States has evolved in the century since the drug was first manufactured. This evolution has occurred in response to government regulations on the production and importation of precursor drugs. An early method of methamphetamine production involved the combination of phenyl-2-propanone (P2P) and methylamine(5). The product was then reduced using a heavy metal to create methamphetamine(9). This method required a greater knowledge of chemistry to accomplish than methods more common now. It also produced both isomers of the drug, requiring an additional purification step to isolate the desired (+)methamphetamine. The method was utilized in larger production laboratories until P2P was listed on the Controlled Substances Act as a Schedule II drug, placing the same restrictions on the sale of P2P as methamphetamine. As the precursor drug became more difficult to obtain and easier methods began to emerge, the P2P method fell in popularity(5).

A second method of methamphetamine production involved reducing (-)ephedrine or (+)pseudoephedrine to (+)methamphetamine

using red phosphorus and hydriodic acid(10). The product was then extracted in its base form and crystalized using hydrochloric acid or hydrogen chloride gas(10). This method was superior to the P2P method as it only produced the more potent isomer of methamphetamine, the precursors were much easier to obtain, and the production required less technical skill than the P2P method.

Related to the red phosphorus method is the Nazi/Birch reduction method. This method also uses pseudoephedrine or ephedrine as a precursor chemical. The necessary reduction is accomplished by the addition of anhydrous ammonia and lithium metal(11). This method has the added benefit of having easily and legally obtained reactants since lithium can be extracted from batteries and anhydrous ammonia is a common industrial fertilizer.

A variation on the Nazi/Birch method is the most commonly found method in the United States today(2). The reaction can take place in one vessel and does not require the addition of external heat, allowing methamphetamine producers to utilize plastic 2 liter bottles as reaction vessels(12). This practice earned the method the new moniker of "one-pot" reaction. The methamphetamine is extracted using a non-polar solvent and crystallized for use(12).

Unfortunately, the method is so simple that many of those who are using it are merely following a recipe, unaware of the dangers of the

chemical reaction they are using. The lithium metal reacts exothermically with water, including the water vapor in air. The heat evolved can ignite the vapors of the highly volatile non-polar solvents causing small explosions or chemical fires.

The potential to cause a fire is not unique to methamphetamine production laboratories. Recently, new facilities have been found that do not produce methamphetamine, but extract it from a solvent in which the drug has been dissolved(2). These "ice conversion" laboratories are a response to drug seizures along the borders where methamphetamine is smuggled(2). Drug traffickers can dissolve the product in a suitable solvent, usually clear, and package the liquid to appear as an innocuous fluid. Once across the border, the solvent is removed. Because methamphetamine is freely soluble in methanol and ethanol, these alcohols are common solvents of choice(2). However, the flammable nature of these chemicals means that these conversion laboratories also have the potential to cause a fire.

1.3 Methamphetamine Detection in Forensic Laboratories

The Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG) has established guidelines for the analysis of controlled substances in forensic laboratories(13). The SWGDRUG criteria for the identification of a seized drug categorizes the common analytical

techniques into three categories according to their potential to uniquely identify a molecule. According to the standard, at least two uncorrelated techniques must be utilized in order to identify a compound, one of which should be from the most discriminatory category(13).

The Gas Chromatograph/Mass Spectrometer (GC/MS) is a hybrid instrument which combines two uncorrelated analytical techniques. Since mass spectrometry is a technique included in the first category of the SWGDRUG guidelines and gas chromatography falls in the second category, identifying seized drugs using the retention time from the GC and the mass spectrum from the MS satisfies the recommendations. This fact, along with the relatively small cost of the GC/MS compared to other analytical instruments and the ability to automate many types of sample injections, has led to the GC/MS being used in many forensic laboratories to identify drugs.

1.3.1 The Mass Spectrometer

Mass spectrometry is a technique designed to identify molecules by determining the molecular weight of their ions. Electron Ionization, or Electron Impact - Mass Spectrometry relies on the predictable fragmentation pattern that molecules produce under specific conditions to determine characteristics about the original molecule, or precursor ion(14). The determination of a molecule's fragmentation pattern, or

mass spectrum, is accomplished in three main steps – the ionization and fragmentation of the molecule into product ions, the separation of the resulting ions, and finally the detection of the ions.

In a mass spectrometer, analytes are ionized within the ion source. Depending on the conditions of this ionization process, the molecule will fragment in a repeatable manner. One common method of effecting this ionization and fragmentation is through electron impact ionization using an electron beam ionization energy of 70 electron volts(15). With this technique, a beam of electrons is directed through the ion source to impact the analytes of interest at a ninety degree angle to the analytes' trajectory. The electrons impart enough energy to the molecules to remove additional electrons creating an unstable positively charged ion. This unstable ion may then fragment into smaller positively charged ions. Ions with a negative charge may also be created depending on the electron affinity of the compound, but positive ion formation is more common. It is also possible for the precursor ion to remain intact depending on its stability(15). Because the fragmentation process is dependent on the strength of the chemical bonds present in the molecule, each chemical will fragment in a manner that reveals information about its original structure.

Once the molecule has been ionized and fragmented, the resulting ions are separated according their mass to charge ratio(14). This

separation occurs in the mass analyzer. Ions can be separated by their relative velocities, as is done in a time-of-flight mass analyzer(16), or by their oscillatory reaction to an electric field, as is done in a quadrupole(17), the mass analyzer used in this study.

A quadrupole is designed with four monopoles aligned in a diamond both parallel to and surrounding the flight path of the ion stream(18). As the ions pass through the center of the quadrupole, a charge difference is induced in the two sets of opposing poles creating two perpendicular dipoles. This causes the charged particles to oscillate in two dimensions as they travel through the quadrupole. Particles with an oscillation of high amplitude will collide with the poles instead of reaching the detector. By constantly changing the charge of the monopoles, the mass analyzer controls when ions of a given mass to charge ratio will be detected. By changing the target mass every few milliseconds, the quadrupole allows the spectrometer to scan for a wide range of masses while still only allowing a narrow range of masses to reach the detector at any one time(18).

The mass to charge ratio of the ions is then determined by when they reach the detector. The detector used for these experiments was an electron multiplier. Electron multipliers work by releasing secondary electrons as the original ion strikes the detector's surface(19). These secondary electrons then strike a second surface either releasing

additional electrons or inducing a phosphor to release light. It is either this light or these final electrons that are detected. The use of an electron multiplier allows a compound to be detected in lower concentrations than would otherwise be possible(19).

The relative abundance of the detected ions is recorded on a mass spectrum. The identity of the original compound is determined by comparing the resulting mass spectrum to spectra of known molecules. Using mass spectrometry can be highly discriminatory because the spectra of all chemical species is unique, with the exception of some isomers(14).

1.3.2 The Gas Chromatograph

As early as 1959, the mass spectrometer was attached to a gas chromatograph to aid in the identification of the components in a mixture(20). Although a mass spectrometer is a powerful tool for the identification of molecules, when multiple compounds are present in a mixture, it can be difficult to identify which compound is creating the ions on the mass spectrum. Gas Chromatography separates molecules based on their physical and chemical properties allowing compounds to enter the mass spectrometer individually(21). The gas chromatograph accomplishes this separation in two main phases – volatilization and through interaction with a stationary phase in a column.

In order for compounds to interact with the stationary phase inside the column, they must be in the gaseous phase(22). Since many samples are introduced into the GC in liquid form, they must first be volatilized. This is accomplished by heating the samples in the sample inlet. The temperature of the inlet can be changed to optimize the vaporization of the analytes. If the inlet temperature is too cool, the compounds will not vaporize and enter the column, but if the temperature is too hot, the compounds may undergo thermal degradation(22).

Once the analytes have been volatilized, they are carried passed a stationary phase within a column using an inert carrier gas, such as helium, nitrogen, or hydrogen(22). Although there are multiple column types including packed columns and capillary columns with a variety of stationary phases, capillary columns are currently used most often. Columns are designed to allow surface interactions with the volatilized analytes without causing chemical changes. As molecules interact with the stationary phase their movement through the column is hindered. Larger molecules and those with a greater affinity for the stationary phase are impeded more than smaller, less attracted molecules. Compounds are identified by comparing how long they are retained on the column to the retention time of a known standard(22).

1.3.3 Sample Preparation

The GC/MS separates and identifies compounds in their gaseous state. Therefore, it is only suitable for compounds that can be volatilized in the inlet. Because the compound of interest in forensic work is often found in non-volatile matrices, the samples must undergo a sample preparation step. The goal of sample preparation is to separate the drug from compounds not of forensic interest. Historically, methamphetamine samples have been prepared for analysis by GC/MS using organic extraction(23), liquid-liquid extraction(24), or solid phase extraction(25). These methods rely on a difference in the affinity of methamphetamine for a solvent or stationary phase over its affinity for the matrix from which the drug is being extracted.

More recently solid phase microextraction (SPME) has been utilized as an extraction method. SPME was developed in 1989 as a method for testing aqueous solutions for specific analytes using GC/MS(26). Although the uses for SPME have grown, only its use as an extraction method for headspace analysis will be presented here. SPME relies on the adsorption of volatile analytes to a polymer-coated fiber. The fiber is exposed to the headspace above the sample in a sealed container. The sample is then heated to allow volatile compounds to be released from the sample into the headspace. As the compounds come in contact with the exposed SPME fiber they can be adsorbed (Figure 1). After the

designated heating time, the fiber is then retracted to prevent desorption of the analytes. The fiber is then re-exposed in the inlet of the GC/MS and heated to allow the captured compounds to be released into the instrument for detection.

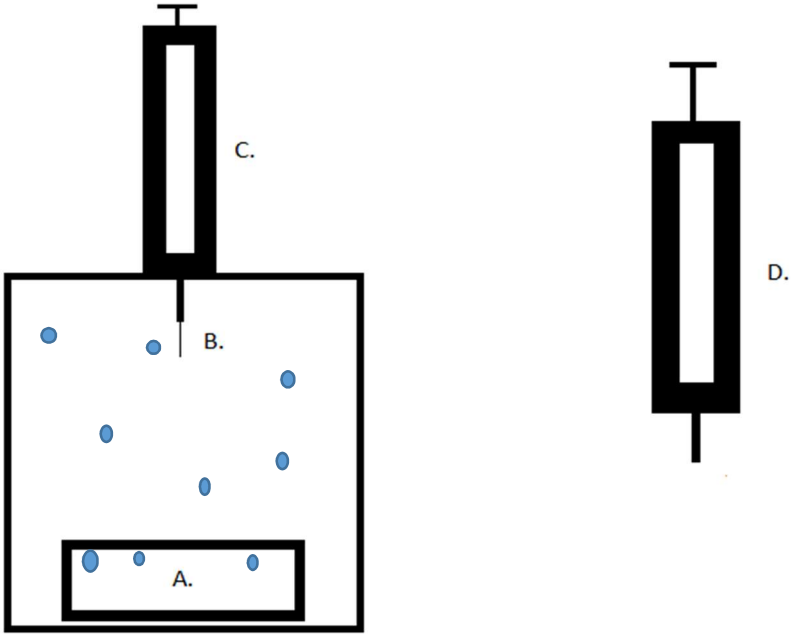

Figure 1. Solid phase microextraction. The Sample (A) is placed in sealed container which can be pierced with a needle. The fiber (B) is exposed to the headspace allowing volatile compounds to be adsorbed. The housing assembly (C) protects the fiber and allows the fiber to be retracted (D) to prevent desorption after analyte collection.

There are a number of advantages to using SPME over the traditional extraction techniques. Because no solvents are used in the analysis, using SPME reduces the amount of chemical waste involved in the analysis process. Only a portion of the target compound is adsorbed to the fiber, leaving the sample behind relatively unaltered for subsequent analysis. There are also a variety of SPME fiber coatings

with various chemical properties. This allows the analyst to choose the fiber with the greatest affinity for the compound of interest, thereby minimizing the collection of other volatile molecules that may be in the sample(27, 28).

One of the drawbacks of using SPME is the difficulty it presents in quantitative analysis. Unlike traditional extraction methods that attempt to recover as much of the drug as possible from the sample in a reproducible manner, SPME samples from the headspace above the sample. The amount of analyte that adsorbs to the fiber can change with temperature, pressure, sample matrix, and the number of volatile molecules competing for the surface area on the fiber. Despite this difficulty, effective SPME methods have been developed for the detection of drugs in saliva(29, 30), hair(31), and urine(32). It has also been shown to effectively detect cutting agents(33) and impurities(34) in seized methamphetamine to aid in determining the source of the drug.

Another drawback is the reusable nature of the SPME fiber. While having a reusable fiber may reduce the cost of each analysis, it also means that the fiber must be cleaned after each use to ensure all compounds have completely desorbed. This not only adds additional time to the analysis, but also prevents sample archiving. The evidence sample itself can be preserved, but the exact conditions of the headspace as they were sampled during the analysis cannot be replicated. In

addition, although the fibers are reusable, they will degrade over time and must be periodically replaced.

1.4 Arson Investigation

The investigation of arson cases can present a unique set of problems because of the destructive nature of the crime. Deciding what is of evidentiary value can be particularly daunting when presented with a scene in which everything is blackened and charred. However, because of the nature of flames, traces of evidence can survive, protected from combustion by the substance that is fueling the fire.

1.4.1 The Nature of Fire

Fire is the perceptible manifestation of a perpetual combustion reaction. Combustion is the exothermic oxidation of organic compounds, i.e. molecules containing chains of carbon-carbon bonds. When these carbon containing compounds contact oxygen molecules with enough kinetic energy, an excess of heat is evolved, imparting additional kinetic energy on the surrounding oxygen molecules and organic compounds which can then collide to continue the process.

For the reaction to continue all three reactants – oxygen, heat and fuel – must be present in sufficient quantities and they must be able to come in contact. Suzanne Bell describes how this requirement of contact

gives evidence the potential to survive a fire in her book *Forensic Chemistry*(21). The fuel that feeds a fire in an arson case is usually found in a solid state. Because of this, only the surface can come in contact with the oxygen in the air to create combustion. As heat is created in the reaction, it pyrolyzes more of the fuel into more volatile decomposition compounds that can vaporize and interact with oxygen. However, as molecules near the surface of the fuel undergo pyrolysis and escape into the gaseous state they take with them the kinetic energy imparted by the heat of combustion. So, although the temperatures near the surface are quite intense, the degradation which the heat causes disproportionately affects the fuel exposed to the air, leaving the fuel underneath protected(21).

Since many of the organic substances found during an arson investigation, like wood and carpet, are porous, they allow other substances to be absorbed into their matrix(35). These absorbed substances can be shielded from the destructive effects of the fire along with the unburnt fuel. This is what allows volatile, flammable liquids to be detected in the laboratory even after surviving intense fires(21).

1.4.2 Detection of Ignitable Liquids

One of the most important questions in arson investigation is how the fire began. An arson in which an accelerant was used will have a

point of origin that shows characteristics of having burned hotter than other parts of the fire. This allows fire investigators a way to potentially identify where they are likely to find traces of the accelerant that remain. Although the volatile liquid can be absorbed into the organic fuel source, once the fire ends, the accelerant will begin to evaporate as normal. In order to preserve the evidence, a sample of the fuel from the point of origin must be sealed into an airtight container, often a metal paint can(36).

There are several methods to analyze fire debris for ignitable liquids including solvent extraction and distillation methods(37). One common method is through passive heated headspace analysis. Using this method the sample can remain in the airtight container. An activated carbon strip is then hung in the container above the sample while the container is heated to allow the volatile liquid to evaporate. The volatile analyte then adsorbs onto the carbon. The strip is then removed from the container and placed in a solvent suitable to desorb compounds, commonly carbon disulfide(38). The resulting solution can then be analyzed by GC/MS.

This method has many of the same benefits as SPME, but in comparing the two methods, passive headspace analysis has one major drawback – carbon's lack of specificity. Unlike SPME fibers which can be designed to have an affinity for a particular type of molecule, carbon strip

chemistry preferentially adsorbs compounds with an affinity for carbon, such as hydrocarbons, whether they be the compounds of interest or those native to the substrate. To compensate for this problem, studies have been done on how to effectively characterize substrate information to better visualize GC/MS information from a possible ignitable liquid(39). Additionally, a database of commonly seen products that interfere with GC/MS analysis in arson cases was created to help investigators identify if their analysis could be confounded by the additional information(35). This database is produced and maintained by the National Center for Forensic Science at the University of Central Florida. Solid phase microextraction has also recently been demonstrated as a possible method of extracting ignitable liquids from fire debris(40, 41).

1.5 Detecting Methamphetamine in Fire Debris

Although arson is defined by the Federal Bureau of Investigation (FBI) as "the willful or malicious burning or attempting to burn…a dwelling house, public building, motor vehicle or aircraft, personal property of another"(42), some states have enacted laws categorizing causing a fire during the production of methamphetamine as arson as well(43, 44). If the fire caused in the clandestine laboratory is extensive, it can destroy much of the evidence that drug manufacturing had taken

place. However, if methamphetamine and its precursor drug, pseudoephedrine, can survive a fire just as ignitable liquids can, their detection would be solid evidence of what was present before the fire.

A recent study at Oklahoma State University was designed to determine whether or not this drug detection was possible(12). The study demonstrated that compounds could be identified on surfaces in a room containing a "one-pot" methamphetamine laboratory after the structure had burned. However, even samples taken from the same surface of the laboratory wall did not all give a positive identification using a passive headspace sample preparation analyzed using a liquid chromatograph/ tandem mass spectrometer. If the conditions that allow the drugs to be detected can be determined, it may give investigators an idea of where to look for evidence in future cases. In addition, if a GC/MS method can be developed using a SPME sample preparation it could be easily implemented in forensic laboratories using the equipment currently available.

2. MATERIALS AND METHODS

2.1 Materials

Pseudoephedrine and Methamphetamine standards were obtained from Cerilliant Corporation (Round Rock, TX). Polydimethylsiloxane/Divinylbenzene SPME fibers (d_f 65µm, needle size 24 ga, StableFlex) were ordered from Supelco (Bellefonte, PA) through Sigma-Aldrich (St. Louis, MO). The solid pseudoephedrine hydrochloride was also obtained through Sigma-Aldrich. The Infrared (IR) Thermometer with a temperature range from -40 °C to 550 °C was obtained from Grainger (Lake Forest, IL). The sample collection cans were made by drilling a hole in the lid of a 1 quart steel can obtained from Fisher Scientific (Waltham, MA) and inserting an 8 mm Precision Seal rubber septum obtained from Sigma-Aldrich. Coleman (Wichita, KS) brand camp fuel and Douglas Fir lumber were purchased from local stores, K-Mart (Somerville, MA) and Home Depot (Watertown, MA) respectively. A BernzOmatic (Columbus, OH) propane torch was used to prepare the burnt samples. An Agilent 7890A GC (Santa Clara, CA) with an attached Agilent 5975C MSD was used to analyze the samples using Chemstation software revision E.02.02.

2.2 Methods

2.2.1 Instrumental Method

The method for detecting methamphetamine and pseudoephedrine in this set of experiments was adapted from that developed for the detection of synthetic cathinones in oral fluid presented by Correll(30). A Polydimethylsiloxane/Divinylbenzene SPME fiber was chosen based on the findings of Koester, Andresen and Grant in their study optimizing the profiling of methamphetamine(28). Although the method changed throughout the course of the experiments to adapt to problems that arose, the following was the standard method used when analyzing the samples. Deviations from this standard are noted in the individual experimental method descriptions.

Prior to sample analysis, the SPME fibers were conditioned by exposure to the GC inlet at 250°C for 30 minutes. All samples were collected into one quart steel cans. The lid of each can had been previously drilled to allow a precision seal septum to be inserted. After the sample had been collected, the lid was tightly sealed. The can was heated in an oven for 10 minutes at 100 °C. The SPME needle was then inserted through the septum and the fiber exposed to the headspace in the can for 10 minutes. After retracting the fiber into the SPME assembly, the needle was removed from the can and

inserted into the injection port of the GC/MS. The fiber was exposed to the inlet for 1 minute to allow the analytes to desorb into the GC. Table 1 shows the parameters used for the Gas Chromatograph.

Table 1. Settings used for the analysis of samples by Gas Chromatograph.

Agilent 7890A parameters		
Injection Method	Manual	
Carrier Gas	Helium	
Inlet Temperature	250 °C	
Oven Temperature Settings	Initial Temperature: 80 °C	Hold for 3 minutes
	Ramp at 40 °C/minute	1.5 minutes
	Ramp at 8 °C/minute	2.5 minutes
	Ramp at 40 °C/minute	3 minutes
	Final Temperature: 280 °C	Hold for 4 minutes
Column	Restek Rxi®-5HT 30 meter 0.25 mmID 0.25 µm df	

The mass spectrometer was run using both Scan and Selected Ion Monitoring (SIM) acquisition modes. The Scan parameters were set to

acquire data from ions with mass to charge ratios (m/z) between 50 and 200. The SIM parameters were set to monitor ions with m/z 58, 91, and 148 starting at 3 minutes and 58, 77, and 105 starting at 6.75 minutes. The SIM parameters were chosen based on the results of the analysis of the methamphetamine and pseudoephedrine standards.

Following the analysis, a cleaning step was implemented to prevent the contamination of subsequent samples. To facilitate this, the fiber was exposed to the inlet of the GC for 5 minutes at 250 °C. During this time the GC oven was set to ramp from 80 °C to 280 °C at a rate of 40 °C/minute.

2.2.2 Characterization of the Components in Wood

Because wood is a complex matrix that may contain compounds that interfere with analysis for possible ignitable liquids(35), unburnt blocks of wood were analyzed to determine what, if any, compounds could be detected in the wood alone. Five blocks of Douglas Fir were cut from an eight foot plank to a size of approximately 3 x 3.5 in. The samples were analyzed using the standard analytical method with one exception. The Scan parameters on the mass spectrometer were extended to include ions with a m/z between 50 and 550. The SIM acquisition mode was not used for this portion of the experiment.

2.2.3 Characterization of Components in Burnt Wood

In order to ensure that the combustion and pyrolysis products of wood would not interfere with the analysis, five blocks of burnt wood were analyzed using the same method as the unburned wood. These samples were prepared using a BernzOmatic propane torch. The flame was passed evenly over the surface of the wood continuously for two minutes while the torch was held approximately two inches from the surface. Samples were allowed to self-extinguish before placing them into the collection can. The samples were analyzed using the same extraction and analytical method as the unburnt samples.

2.2.4 Identification of Methamphetamine and Pseudoephedrine on Burnt Wood

To determine whether the compounds identified in wood would interfere with the detection of methamphetamine and pseudoephedrine, the blocks of wood previously burned and analyzed were spiked with 250 µL of pseudoephedrine and methamphetamine standard. The standards had a concentration of 1 mg/mL. The samples were then reanalyzed to verify that the two compounds could be identified from the matrix.

2.2.5 Burning Trace Quantities of Methamphetamine and Pseudoephedrine

For this experiment, varying quantities of methamphetamine and pseudoephedrine dissolved in methanol were spiked onto approximately 3 x 3.5 in. blocks of wood. Approximately 1.5 mL of Coleman camp fuel was added to each of 50 blocks. Ten blocks contained neither drug, ten were spiked with 100 µg of each, ten with 250 µg, ten with 500 µg, and a final ten with 1 mg of each drug. A fire was created in a burn vessel at the Boston University Holliston research facility. The blocks of wood were placed on a grate suspended above the fire and allowed to burn for 10 minutes. The temperature of the fire was measured and recorded periodically using an IR thermometer. The blocks were then removed from the fire and allowed to self-extinguish. All samples were analyzed using the standard extraction and analytical method described in the instrumental method section.

2.2.6 Detecting Pseudoephedrine

Because solid dose pseudoephedrine is not as volatile as either the base form or the drug dissolved in methanol, 5 mg of solid dose pseudoephedrine were placed on both unburnt and burnt wood blocks to analyze what effect this difference would have on detection. These samples were tested using the extraction and analytical method

described in the instrumental method section. According to a study by Wille and Lambert, ephedrine, the stereoisomer of pseudoephedrine, can be misidentified as phenmetrazine if the drug can interact with formaldehyde while in the inlet of the GC/MS(45). Because the burned samples were not identified as pseudoephedrine using a library search, but rather as phenmetrazine, the samples were tested again using variations on the standard method with lower inlet temperatures. The samples in question, as well as a sample from an unopened vial of the pseudoephedrine standard in methanol were analyzed three times using different inlet temperatures. The first analysis used an inlet temperature of 50 °C; the second, 150 °C; and the third, 250 °C.

2.2.7 Detecting Burnt Pseudoephedrine

The purpose of this experiment was twofold. The first goal was to identify how much pseudoephedrine hydrochloride must be present before a fire for the drug to be detected after the fire. The second was to determine if the drug being dissolved in methanol before the fire would help or hinder its detection.

Three quantities of crystalline pseudoephedrine were tested; 5 mg, 15 mg and 25mg. Three blocks of wood were prepared for each quantity using pseudoephedrine in its solid form. An additional three samples for each quantity were made by dissolving the drug in 1 mL of methanol and

pouring the resulting solution on the blocks of wood. Each sample was then burned separately for two minutes using a BernzOmatic propane torch in the same manner as before. Data concerning the temperature of the fire on the surface of the wood was collected using an IR thermometer.

3. RESULTS

3.1 Characterization of the Components in Wood

In order to determine the compounds endogenous to the Douglas Fir planks, five blocks of wood were analyzed. No two blocks of wood produced the same chromatogram, however similar compounds were found in multiple blocks of wood. Palmitic acid, also known as n-hexadecanoic acid, has a retention time of 9.7 minutes and was detected in four of the five samples and the most abundant compound in those samples. Eugenol was detected in two of the five samples. It has a retention time of 7.5 minutes. A series of hydrocarbons was also detected in three of the five samples with a retention time of 10.6 minutes. Each subsequent peak elutes approximately 25 seconds from the preceding peak. The pattern can be seen in the representative chromatogram (Figure 2). Although the origin of this hydrocarbon series was not determined, for this study it was considered a component of the processed wood due to its presence in a majority of these samples and all subsequent samples.

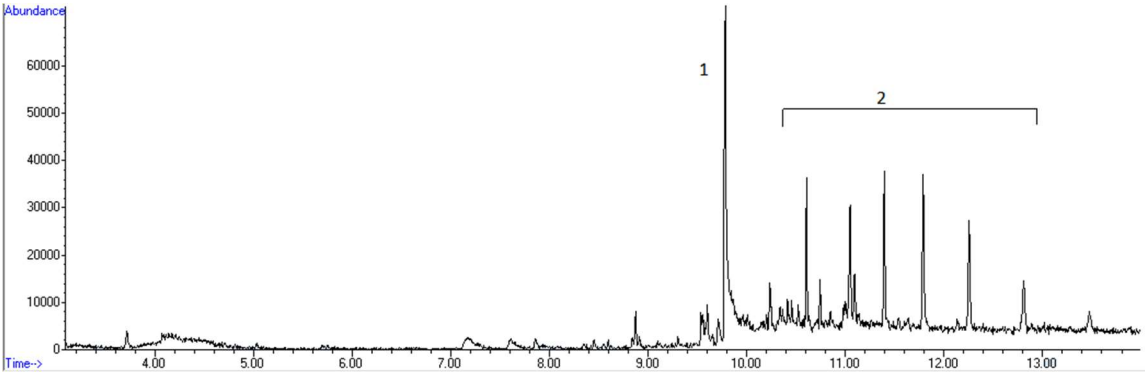

Figure 2. A chromatogram produced from analyzing Douglas fir. Peak 1 is palmitic acid. The series of peaks marked 2 are hydrocarbons. Eugenol was not detected in this sample, but was seen in two samples at the 7.5 minute mark.

3.2 Characterization of Burnt Wood

The same five samples of wood previously analyzed to identify the components of unburnt wood were further evaluated after they had been subjected to the flame of the BernzOmatic torch for two minutes. The same compounds present in unburnt wood were also detected after the burning process. The hydrocarbon series seen in three of the five unburnt samples was detected in all five burnt samples. In addition to the palmitic acid, eugenol and hydrocarbons, other compounds were also detected, however they were not present in all samples. The abundance of each "new" peak was determined to be less than 25% of the base peak, either palmitic acid or eugenol. A list of compounds detected in the burned wood samples along with their retention times and most abundant fragment ions was compiled (Table 2).

Table 2. A list of compounds detected in burnt wood. Compounds are listed in order of retention time. Each was identified by comparison to the 2005 NIST Mass Spectral Library.

Retention Time (minutes)	Compound Name	Mass Fragments (m/z)
3.63	β-pinene	93, 69, 77
4.59	Guaiacol	109, 124, 81
5.38	Creosol	138, 123, 98
5.68	Benzothiazole	135, 108, 69
6.07	p-ethylguaiacol	137, 152
6.37	p-vinylguaiacol	150, 135, 107
6.38	phthalic anhydride	104, 76, 148
6.73	Eugenol	164, 149, 77
7.11	Vanillin	151, 150, 73
7.13	4-Isopropoxybutanol	55, 73, 89
7.14	β-elemene	81, 93, 67
7.53	Iso-eugenol	164, 149, 77
7.89	β-selinene	105, 93, 80
7.95	α-selinene	189, 93, 107
8.89	Stearic acid	73, 57, 129
9.10	Tetradecanoic acid	73, 60, 129
9.79	Palmitic acid	73, 55, 129, 256
10.73	Tributylacetylcitrate	185, 259, 129
11.05	Heptacosane	57, 71, 85
11.40	Octacosane	57, 71, 85

3.3 Identification of Methamphetamine and Pseudoephedrine on Burnt Wood

The methamphetamine spiked on the burnt wood was detectable in all five samples in varying abundance. In two of the samples, methamphetamine was the most abundant compound detected. In a third, the methamphetamine peak has a relative abundance 25% as large as the base peak, palmitic acid. The final two samples had a relative abundance less than 5% of the base peak. Methamphetamine has a retention time of 5.32 minutes using this method and is baseline resolved from the two closest compounds detected in burnt wood, creosol and guaiacol.

Pseudoephedrine was detected in only three of the five samples when added to previously burned wood. In those three samples it was detected at the same relative abundance as methamphetamine. It has a retention time of 6.93 minutes and is resolved from the two closest peaks present in the burnt wood, eugenol and vanillin. A chromatogram of methamphetamine and pseudoephedrine spiked on burnt wood is presented (Figure 3).

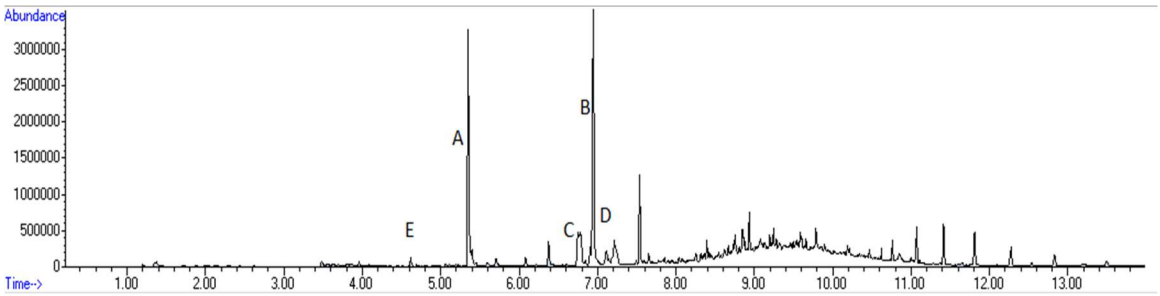

Figure 3. Chromatogram of methamphetamine (A) and pseudoephedrine (B) on burnt wood. They are chromatographically resolved from the detectable compounds of burnt wood eugenol (C), vanillin (D) and guaiacol (E).

3.4 Burning Trace Quantities of Methamphetamine and Pseudoephedrine

The samples containing less than 1 mg of pseudoephedrine and methamphetamine were burned for 10 minutes. The temperature of the fire in which the samples were burned was not consistent throughout the experiments. The fire periodically exceeded the detection range of the thermometer, 550 °C. Temperatures were taken as the wooden blocks were placed into the flame and five minutes into the burning period. All

temperatures exceeded 340 °C with a median initial temperature of 525 °C. The median temperature taken after five minutes of burning was 521 °C with all temperatures exceeding 400 °C.

Neither methamphetamine nor pseudoephedrine was detected in any of the forty samples or ten blanks that were prepared in this manner. Traces of the ignitable liquid, Coleman camp fuel, were detected in the samples, however the chromatographic data would not be sufficient to identify the liquid in an unknown sample. A representative chromatogram from these samples is presented (Figure 4).

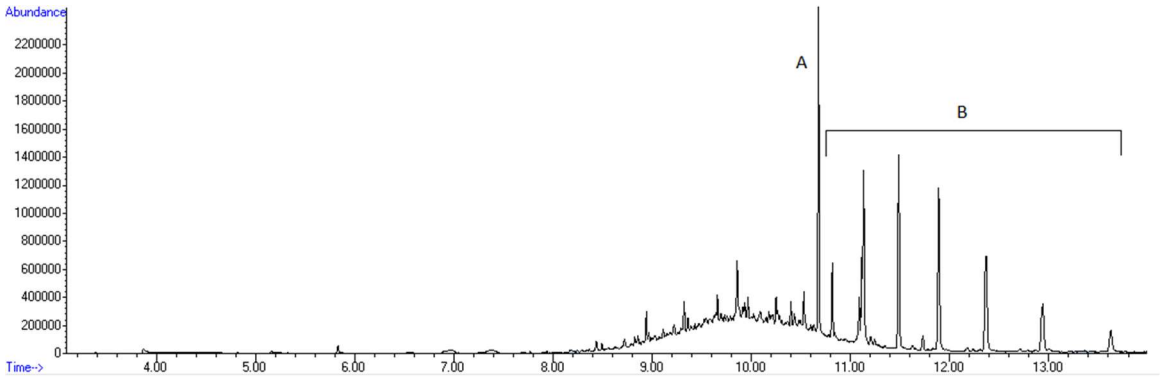

Figure 4. Chromatogram of a sample with 1 mg of pseudoephedrine and methamphetamine standards burned for 10 minutes. The identifiable peaks are tributylacetylcitrate (A) and a series of hydrocarbons (B).

3.5 Detection of Pseudoephedrine

The comparison between the detection of pseudoephedrine hydrochloride powder and the powder dissolved in methanol resulted in a higher detection of the solid form than the dissolved state. A

chromatographic comparison of the two when analyzed on unburnt wooden blocks is given in figure 5.

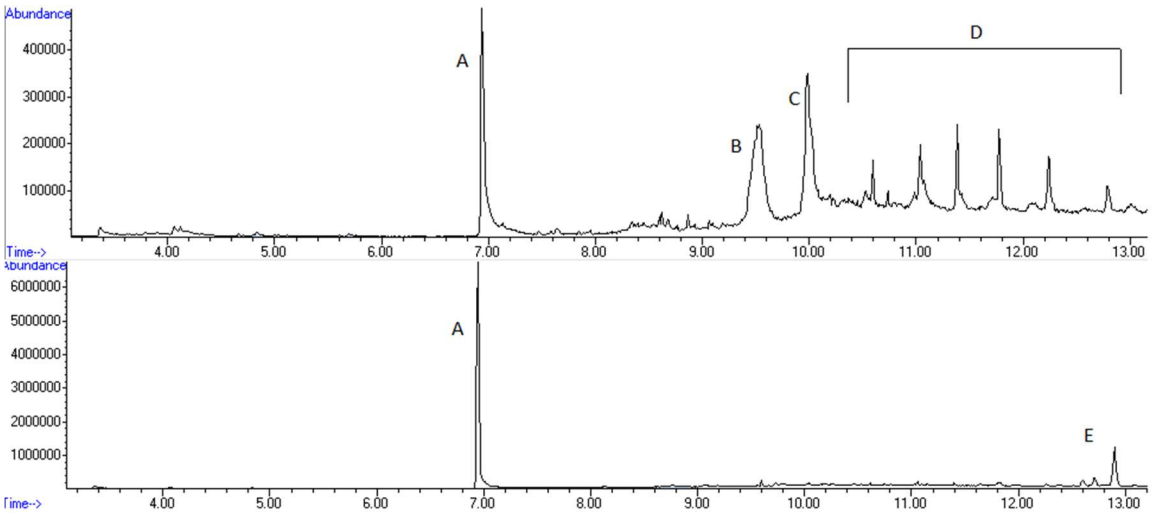

Figure 5. Comparison of chromatograms generated from pseudoephedrine dissolved in methanol (Top) and pseudoephedrine powder (Bottom) each spiked on an unburnt block of wood. The identified peaks are pseudoephedrine (A), palmitic acid (B), and a series of hydrocarbons (D). The peaks labeled C and E were unidentifiable by spectral library search.

The pseudoephedrine standard and the pseudoephedrine hydrochloride which had been burned gave different mass spectral results. The first had a base peak of 58 m/z and ions detected with m/z 77 and 91. The burned pseudoephedrine hydrochloride had a mass spectrum with a base peak of 71 m/z and an ion with m/z 56. Therefore, an attempt was made to determine what could cause the change in detected mass fragments. A comparison of pseudoephedrine hydrochloride powder in three forms is shown in Figure 6. The first form is before it has been heated. The second is the result of heating 10 mg

for ten minutes at 200 °C in an oven. The third form was detected after heating 10 mg for one hour at 200 °C.

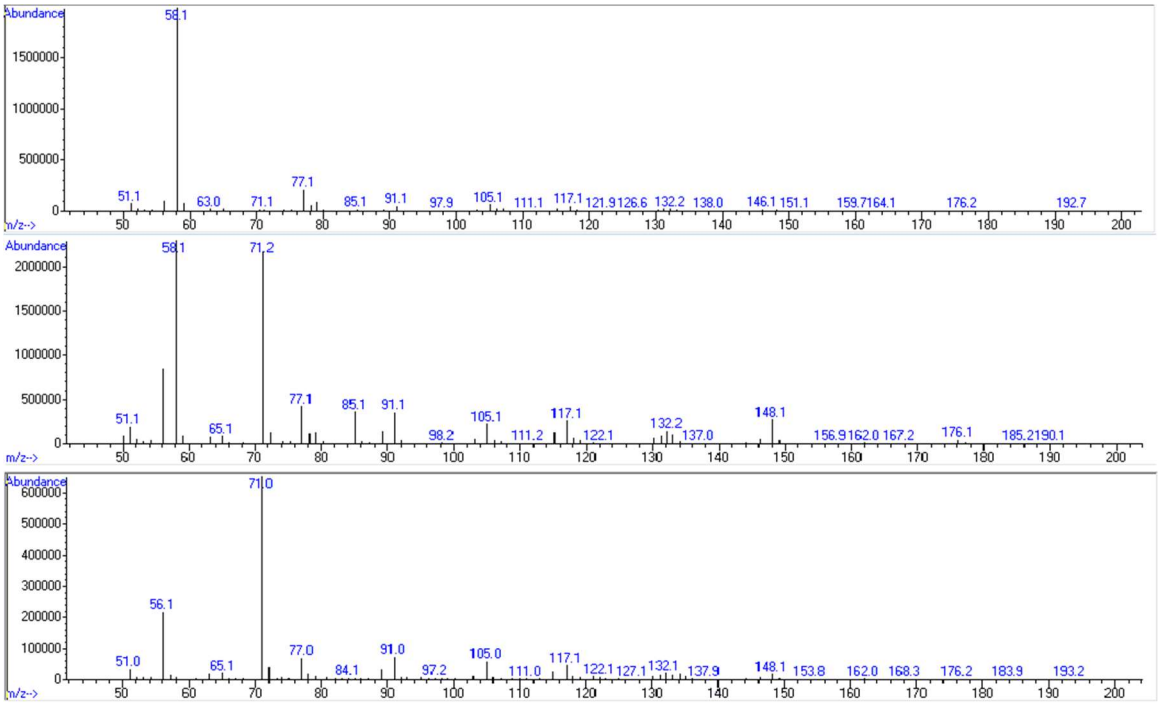

Figure 6. Comparison of 10 mg pseudoephedrine mass spectra. The top spectrum is pseudoephedrine powder stored at room temperature. The middle spectrum was obtained after heating that powder for 10 minutes at 200 °C. The bottom spectrum was obtained when analyzing the sample after heating for 1 hour at 200 °C.

The inlet temperature comparison study revealed no differences in results dependent on GC inlet temperature. All samples and standards tested gave the same mass spectral results at all three inlet temperatures, 50°C, 150°C and 250 °C. A portion of the pseudoephedrine was detected as carryover in the blanks following the samples analyzed using a 50°C inlet temperature. Therefore, all subsequent analysis was performed using the original inlet temperature, 250 °C.

3.6 Detecting Burnt Pseudoephedrine

The samples containing 5 mg, 15 mg or 25 mg of pseudoephedrine were burned for a period of two minutes in a controlled laboratory setting. The surface temperature of the burning blocks of wood was taken at both thirty and ninety seconds into the burning process for the samples containing 15 mg of pseudoephedrine. The surface temperature was highly variable and dependent on the proximity of the measured surface to the torch. At thirty seconds, the temperatures ranged from 200 °C to 480 °C. At ninety seconds the temperature had increased to a range from 320 °C to above the thermometer's detection limit of 550 °C.

Pseudoephedrine was not detected in any of the samples prepared with 5 mg, 15 mg or 25 mg of the drug. However all of the samples that had been prepared with 15 mg or 25 mg of pseudoephedrine did contain a compound with the same retention time as pseudoephedrine and with a mass spectrum similar to that of pseudoephedrine that has been degraded at high temperature. An additional peak was detected in the samples containing 25 mg of pseudoephedrine at a retention time of 9.21 minutes displaying a similar mass spectrum. A representative chromatogram with mass spectra is included in Figure 7.

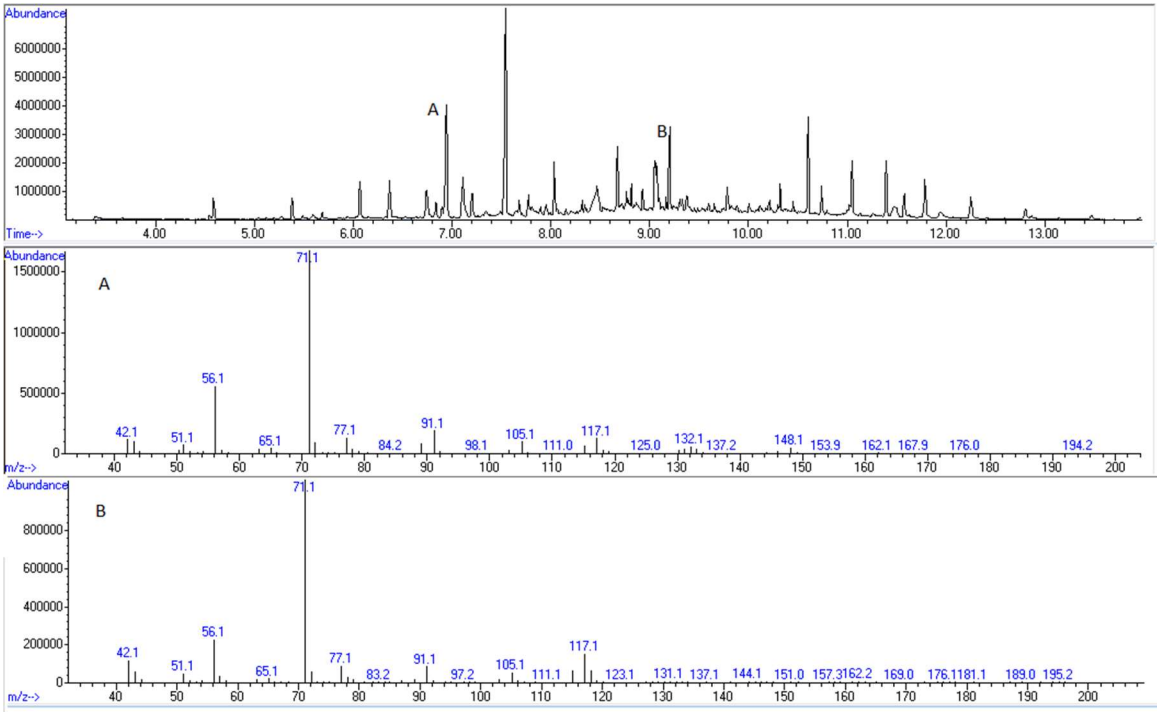

Figure 7. Chromatogram of a sample prepared by burning 25 mg of pseudoephedrine on a wood block. Mass spectra for the peak that elutes at the same time as pseudoephedrine (A) and for a peak at 9.21 minutes with similar fragments (B) are shown.

4. DISCUSSION

4.1 Advantages of the SPME GC/MS Method

Implementing solid phase microextraction for sample preparation in laboratories can provide several advantages. SPME eliminates the use of solvents in the sample preparation process, reducing waste and exposure to potentially hazardous chemicals. The extraction technique is simple and SPME requires limited specialized knowledge and skills, and can be analyzed using equipment already commonly available in many laboratories. It can be quickly and easily implemented in forensic laboratories. The extraction process is also relatively quick since the only sample preparation is the incubation time. The extraction can also be optimized to the drugs by choosing the correct SPME fiber. A fiber with a high affinity for pseudoephedrine and methamphetamine and low affinity for hydrocarbons would reduce the competitive adsorption faced by activated carbon strips with their high affinity for hydrocarbons.

The analytical method presented also has several advantages because of its use of GC/MS. This instrument is widely used in forensic laboratories. Therefore, the initial costs of implementing this method could be minimalized. Additionally, analysts would not need to be trained in the use of a new instrumentation. Most significantly, this GC/MS method can be optimized to simultaneously detect methamphetamine and pseudoephedrine in samples that may contain

complex matrices and volatile ignitable liquids. Although a different technique would need to be employed to confirm the identity of an ignitable liquid, the possible presence of three components of the clandestine manufacture of methamphetamine can be screened at once; the product drug, precursor drug, and common production solvents. The fact that the pseudoephedrine and methamphetamine peaks are chromatographically resolved from compounds in the matrix allows for one of the method's biggest advantages. Analysis can be performed without changing the original sample, effectively leaving any evidence items intact.

4.2 Disadvantages of the SPME GC/MS Method

A drawback of using this method is the inability to quantitate the results. The amount of the analyte that adsorbs to the SPME fiber is dependent not only on the temperature and the analyte concentration in the headspace, but also on the concentration of competing compounds. Because there is limited space on the fiber, molecules can displace one another. An increase in the concentration of palmitic acid, eugenol or the presence of an ignitable liquid with an affinity for the chosen SPME fiber, could potentially displace more of the pseudoephedrine, causing a decrease in detection even though the actual concentration remained constant.

This method also requires manual injection into the GC inlet. This lack of automation greatly reduces the efficiency of the method. Unlike solvent based extraction techniques which can be used to prepare a large number of samples and paired with an autosampler, this method requires an analyst to be present to start the next step of the process every ten minutes. While this may represent a minor inconvenience in analyzing a handful of samples, it could represent an overwhelming burden in high through-put laboratories.

The fact that SPME fibers are reused can also present a problem in a forensic setting. The fiber must be cleaned after each sample by thermally desorbing any residual analytes from the fiber. This process prevents carryover between samples, but it also prevents sample preservation for later testing. Although the evidence sample is left intact, the process of extraction removes a portion of the volatile organic compounds from the headspace. In samples involving trace amounts of pseudoephedrine, the change in headspace composition may be significant. Using an activated charcoal strip to analyze the headspace allows an analyst to cut the strip in sections leaving a portion of the charcoal strip for retesting. This practice allows any subsequent analysts to test the components of the headspace exactly as it existed for the first analyst. Such preservation is not currently possible with SPME.

Finally, SPME fibers can be expensive. The fibers used for this study cost approximately $450 for three. This expense can be exacerbated by the fragile nature of the fibers. Fibers will degrade with use as they are exposed to the heat of the GC inlet. The coating on the fiber is also easily removed if the fiber is mishandled when exposing the fiber either in the headspace or in the inlet. Replacing these fibers may represent a significant cost in laboratories utilizing this technique.

4.3 Confirming the presence of Pseudoephedrine

SWGDRUG standards require that two different analytical techniques be used to confirm the identity of an unknown drug.(13) If unknown samples contained ≥15 mg of pseudoephedrine, the combination of GC with MS would be necessary to confirm the compound as pseudoephedrine. The difference in the mass spectrum would preclude the confirmation of the drug's identity. However, just as drug metabolites in bodily fluids can be used to confirm that certain drugs had been taken previously, with further investigation pyrolysis products could potentially be used to identify that a drug had been present before a fire. This would require that the pyrolysis products be shown to be unique to the drug in question. Unfortunately, although the pseudoephedrine degradation experiment shows that pseudoephedrine, when heated above 200 °C in an oven, will give results similar to those of

the pseudoephedrine in the fire, it is not sufficient to prove that a peak detected at 6.93 minutes on a chromatogram using this method and also having a mass spectrum with mass fragments with m/z 71 and 56 is confirmation that pseudoephedrine had been present.

4.4 Further Research

Although the research presented here provides a basis for considering SPME to detect pseudoephedrine in fire debris, more research is needed before the results of this controlled study can be applied to real world situations. The following list of research ideas is an attempt to highlight those questions which, when answered, could solidify or call into question the findings of this study.

4.4.1 Optimization of the SPME fiber

The SPME fiber used in this study, a Polydimethylsiloxane/Divinylbenzene coated fiber, was chosen based on research intended to optimize the detection of methamphetamine and its impurities(28-30). It is possible that the optimal fiber for detecting methamphetamine is also the optimal fiber for detecting the components of wood which may displace the drug from the SPME fiber. If this is the case, the best fiber for detecting drugs in fire debris may be one that has a lower adsorption efficiency for methamphetamine alone, but a higher

adsorption efficiency for methamphetamine in this matrix. If a fiber with this selectivity does exist, it may be the more efficient extraction fiber.

4.4.2 Is the Overall Analytical Approach Effective in Other Matrices?

While wood is a common building material, it is not the only substrate to survive a fire nor the only type of evidence submitted in an arson investigation. In addition, only one type of wood was tested in this study. Other substrates may have different volatile components that would adsorb to the SPME fiber using these extraction conditions. The method used here effectively separates the two drugs from the compounds in Douglas Fir. The same method may result in the drugs' elution at the same time as components in other substrates. Additionally, the wood used in this study provides an absorbent material that may be sheltering a portion of the drug within its matrix. It is unclear, however, whether drugs on a less porous substrate could be detected.

4.4.3 How long can Pseudoephedrine Last in a Fire?

Only two burning times were tested in this study, two minutes and ten minutes. The quantity of drug used in each portion of the study was substantially different, so their results cannot be compared directly. 15 mg was a sufficient quantity for a possible product to be detected after

two minutes. Could a similar detection be made if the fire had lasted for ten minutes? In fires that are not extinguished in the ten-minute time frame, is it feasible to look for traces of the drug under these conditions?

4.4.4 What are the Pyrolysis Products?

The results of this study indicate that pseudoephedrine may thermally degrade under high heat conditions into a substance with a similar retention time that has a different mass spectrum. Is this a pyrolysis product of pseudoephedrine that could be expected to be seen any time the drug is heated or does it only occur in certain situations? More importantly, if this is a product of heating, is it unique to pseudoephedrine or is this a common product of burning drugs of this class. Similarly, if this change of structure occurs when heating pseudoephedrine, does a similar reaction occur to methamphetamine?

4.4.5 Can Burned Methamphetamine be Detected?

Although preparatory testing was done in this study to show the possibility that it may work in detecting methamphetamine in fire debris, testing the theory with the solid dose drug could not be performed. This information is vital to determining if the method is feasible for use in evidence analysis. Detecting the final product gives a much stronger

indication of what was happening before a fire than detecting the precursor alone or even the precursor and extraction solvent.

5. Conclusion

The use of SPME as a preparation step for detecting pseudoephedrine and methamphetamine by GC/MS does show potential. It allows for a quick, easy, and non-destructive preparation without the use of hazardous solvents. However, the cost of replacing the SPME fibers and the fact that a portion of the sample tested cannot be archived for retesting may be significant factors to dissuade forensic laboratories from implementing SPME techniques for fire debris analysis.

The described GC/MS instrumental method demonstrates that methamphetamine and pseudoephedrine can be baseline resolved from each other as well as from components of a wooden substrate. Although the instrumental method could not be used to identify the ignitable liquid, the presence of that liquid would not interfere with the identification of methamphetamine or pseudoephedrine.

Finally, it was demonstrated that pseudoephedrine thermally degrades when exposed to temperatures above 200 °C. This degradation occurred in the absence of any solvents. The product of this degradation is consistent with the compound detected in fire debris from wood spiked with pseudoephedrine. This compound, having the same retention as pseudoephedrine on a gas chromatogram and a mass spectrum with a base peak of 71 m/z and a 56 m/z ion at approximately fifty percent of

the base peak abundance, is therefore presented as a possible indicator of pseudoephedrine when detected in fire debris.

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Curriculum Vitae

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Educational Background

Boston University Anticipated Graduation: May 2016
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M.S. Biomedical Forensic Science

Brigham Young University August 2012
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Utah Valley State College August 2006
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Relevant Experience

Boston University August 2015 - Present
Research Assistant

- Perform routine maintenance and troubleshooting on an Agilent GC/MS
- Perform routine maintenance and troubleshooting on a Shimadzu Prominence UFLC and AB SCIEX 4000 Qtrap
- Maintain safety data sheets (SDS) and certificates of analysis for laboratory chemicals
- Assist in research of other graduate students and their training
- Ensure proper storage and disposal of laboratory chemicals

Utah Valley University January 2014 - May 2014
Laboratory Assistant

- Prepared laboratory experiments for first year undergraduate laboratories in the chemistry department
- Ensured proper storage and disposal of laboratory chemicals
- Prepared and maintained safety data sheets for laboratory chemicals
- Performed troubleshooting on an Agilent GC/MS

American Preparatory Academy August 2012 - June 2013
Chemistry/Latin Teacher

- Created curriculum for and taught the first year chemistry course
- Prepared reagents for the chemistry laboratory
- Maintained the laboratory for the chemistry department
- Taught first and second year Latin courses

Utah Valley University December 2013 – May 2014
Research Assistant

- Extracted atranorin from lichen samples for HPLC analysis
- Determined the total protein content of lichen samples
- Reviewed abstracts for presentation submission

Scholarships

Boston University
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